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Fluid Phase Equilibria

Micellization properties and related thermodynamic parameters of aqueous sodium dodecyl sulfate and sodium dodecyl sulfonate solutions in the presence of 1-propanol

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ABSTRACT

Effects of 1-propanol (1P) addition on the micellar and thermodynamic parameters of aqueous solutions of anionic surfactants sodium dodecyl sulfate (SDS) and sodium dodecyl sulfonate (SDSn) was investigated by experimentally measured electrical conductivities, densities and sound velocities at 298.15 K. The values of the critical micelle concentration (CMC) of both surfactants in the investigated mixed aquo-1P solvents (wt% 1P 2.5, 5, 7.5 and 10) are smaller than those in pure water and the CMC decreases with increasing 1P concentration in solution to a minimum at (w/w) % 1P = 5 and then increases. However the values of the counterion condensation on the micelle decrease with an increment in the amount of 1P. Furthermore the values of the apparent molar volume and isentropic compressibility of the monomeric and micellar forms of the investigated surfactants were obtained from the experimental density and sound velocity data. It was found that, although the values of the apparent molar properties of micellar form of surfactants increase by increasing the organic solvent content, the values of the apparent molar volume of the monomeric form of the surfactants decrease with increasing concentration of 1P.

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1. Introduction

The aqueous solutions of surfactants have important properties for a wide range of both industrial and everyday life application fields and their properties have received considerable attention. In aqueous solutions, amphiphilic molecules of surfactants self-aggregate together to minimize the contact area of the hydrophobic segment and water and form different types of aggregates. The aggregation behavior of surfactants in aqueous solutions is significantly influenced by solvent properties such as the polarity, hydro- and lipophilicity, hydrogen-bonded structure, and fluidity which can be controlled/varied by adding different amounts of a cosolvent or a cosurfactant to the aqueous solution. In fact, the tendency of the surfactants molecules to avoid contact with the water can be altered by the addition of polar organic solvents to the aqueous micellar solutions and therefore, it is expected to affect the values of the critical micelle concentration (CMC), the degree of ionization of the micelles, aggregation number and thermodynamic properties of the monomeric and micellar forms of surfactants. In the other

words, the introduction of additives provides additional degrees of freedom with which to control the self-aggregation of surfactants and the properties of the resulting formulation [1] and therefore such investigations are necessary for the optimum utilization of amphiphiles in industrial, medicinal, and pharmaceutical fields in relation to emulsification, stabilization, extraction, cosmetic formulation, drug encapsulation, and synthesis of nanomaterials [2]. Furthermore such studies have potential use in food applications [3–10].

Alkanol additives to aqueous surfactant solutions can be classified into cosolvents and cosurfactants [11]. The alkanols higher than propanol normally act as a cosurfactant and decrease the CMC by their presence. Cosurfactants cannot form micelle alone, but they adsorb at the outer portion of the micelles, decreasing the repulsive interactions between the ionic heads and therefore they favor micellization of the surfactants. Methanol which is the smallest alkanol behaves like a cosolvent in water and decreases the dielectric constant of the medium and favorites the water–surfactant interactions which therefore results in increasing the CMC of surfactants in aqueous solutions. Ethanol and propanol show a dual property of both cosurfactant and cosolvent behavior so that they act as a cosurfactant and reduce the CMC at low concentration whereas they increase the CMC at high concentration, indicating theirs role as cosolvent [1,12,13].

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Among all the surfactants in the mixed aquo-organic solvents, sodium dodecyl sulfate (SDS), is the most studied anionic surfactants and its micellization in water–organic solvent mixtures has been studied extensively by different research groups [2,12,14–23]. However for sodium dodecyl sulfonate (SDSn) which has a similar structure with SDS, as far as we know there is no information in the literature. Furthermore information about the volumetric and compressibility properties of anionic surfactants in the mixed aquo-organic solvents is scarce in the literature. The only difference between these two anionic surfactants is in an oxygen atom and therefore, comparison between thermodynamic properties of these surfactants in mixed aquo-organic solvents is interesting and can provide extensive information about solute–solute and solute–solvent interactions of the surfactants in solution. These have convinced us in studying the micellization behavior and evaluation of associated parameters of anionic surfactants SDS and SDSn in water-1-propanol (1P) mixed solvent system. In this study, the effects of 1P addition on the micellar and thermodynamic parameters of aqueous solutions of SDS and SDSn were investigated by experimentally measured electrical conductivities, densities and sound velocities at 298.15 K. This study for the first time provides the differences between SDS and SDSn, with respect to their thermodynamic properties, micellization and different interactions in the mixed aquo-organic solvents.

2. Materials and methods

2.1. Materials

SDS (purity > 98%), SDSn (purity > 99%) and 1-propanol (purity > 99.8%) were obtained from Merck and were used without further purification. The aqueous solutions of the surfactants and 1P mixture were prepared using doubly distilled and deionized water.

2.2. Methods

Conductometry measurements were made with a digital conductometer (Metrohm model 712) using a dipping-type conductivity cell with platinized electrodes at a frequency of 1 MHz. All measurements were performed in a double-walled glass container at 298.15 K maintained by a Julabo circulating thermostat with a precision of 0.02 K. A concentrated surfactant solution was progressively added to a known quantity of a mixed (water-1P) solvent taken in the container.

Density and sound velocity measurements were carried out by an Anton Paar DSA 5000 model high precision vibrating tube digital densimeter and sound velocity measuring device, with automatic viscosity corrections and proportional temperature control that kept the samples at working temperature within $\pm 10^{-3}$ K. The calibration of the instrument was made with degassed and bidistilled water and dry air at atmospheric pressure according to the instruction manual of the instrument. The uncertainties of measurements were $\pm 5 \times 10^{-6}$ g cm^{-3} for density and $\pm 10^{-1}$ m s^{-1} for sound velocity. All the solutions for density and sound velocity measurements were prepared by mass on a Sartorius CP225D balance precisely within $\pm 1 \times 10^{-5}$ g.

The apparent molar volumes, V_ϕ, and isentropic compressibilities, K_ϕ, were calculated by means of the following equations.

$$V_\phi = \frac{M}{d} - \frac{1000(d - d_0)}{mdd_0},\tag{1}$$

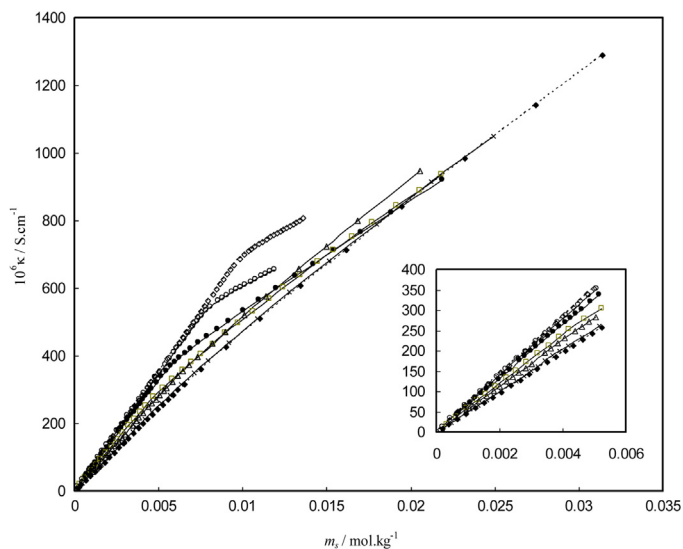$$K_\phi = \frac{M\kappa_s}{d} - \frac{1000(d\kappa_{s0} - d_0\kappa_s)}{mdd_0}\tag{2}$$

Fig. 1. Plot of specific conductivity data, κ, against molality of solute, m, at 298.15 K: ○, SDS in water; ●, SDS in aqueous solutions of 2.5%wt 1P; □, SDS in aqueous solutions of 5%wt 1P; △, SDS in aqueous solutions of 7.5%wt 1P; ×, SDS in aqueous solutions of 10%wt 1P; ◇, SDSn in water; ◆, SDS in aqueous solutions of 10%wt 1P.

where d is the density of a solution of molality m, M is the molecular weight of the surfactant, d_0 is the density of the solvent. κ_{s0} and κ_s are the coefficients of isentropic compressibility of the solvent and solution, respectively. Isentropic compressibility κ_s (kPa)$^{-1}$ is calculated from sound velocity, u, and density data as

$$\kappa_s = \frac{1}{du^2}\tag{3}$$

3. Results and discussion

In this study, in order to study how the solvent media influence the micellization of the anionic surfactants and to explore the differences between SDS and SDSn with respect to their micellar and thermodynamic parameters in the mixed aquo-organic solvents, electrical conductivities, densities and sound velocities of solutions of SDS and SDSn in water and in aqueous solutions of 2.5, 5, 7.5 and 10%wt 1P were determined at 298.15 K. The measured experimental data are reported in Tables 1–4.

As a representative example, Fig. 1 shows the plots of specific conductivity vs. molality of SDS and SDSn in aqueous 1P solutions at 298.15 K.

Distinct break points in the conductivity vs. molality were observed as the CMC and are given in Table 5. As can be seen from Fig. 1, this break point in the conductivity profile becomes less distinct as the concentration of 1P increases. It can be seen that the addition of 1P in water leads to a decrease in the CMC up to 5%wt 1P and beyond that the values of CMC increase by increasing 1P concentration in solution. Micellization of ionic surfactant in aqueous solution results from a balance between two opposing interactions [24]: (1) electrostatic repulsion between the ionic head groups which disfavors micellization and (2) attractive hydrophobic interaction involving the alkyl chains which favors micellzation. For all the investigated mixed aquo-1P solvents (wt% 1P 2.5, 5, 7.5 and 10), reducing the former interactions in the presence of 1P is dominant contribution and increases up to 5%wt 1P and therefore the values of CMC of both surfactants in the investigated mixed aquo-1P solvents are smaller than those in pure water and decrease with increasing 1P concentration in solution to a minimum at (w/w) % 1P = 5 and then increases. In fact the former interaction can be reduced by incorporating of 1P into micelles thereby decreasing the repulsive interactions between the ionic head groups, lowering